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## KINETIC STUDIES ON FAST REACTIONS IN SOLUTION VI

The Kinetic Studies on the Reaction between Tetrahalogeno-*p*-benzoquinones and Alkali Iodides

BY MUNEO SASAKI

The reactions to produce the semiquinone ion radicals by the electron transfer between tetrahalogeno-*p*-benzoquinones (fluoranil, chloranil, bromanil and iodanyl) and alkali iodides (NaI and KI) were investigated photometrically in acetone solution in the temperature range, 20°~35°C, from the view point of kinetics. The rate of semiquinone ion radical formation is of first order for *p*-benzoquinones and of second order for alkali iodides. Activation energies and entropies are as follows: for chloranil-NaI,  $\Delta E^\ddagger = 6.8$  kcal/mole,  $\Delta S^\ddagger = -19.4$  e.u.; for chloranil-KI,  $\Delta E^\ddagger = 7.6$  kcal/mole,  $\Delta S^\ddagger = -18.6$  e.u.; for bromanil-NaI,  $\Delta E^\ddagger = 9.7$  kcal/mole,  $\Delta S^\ddagger = -16.6$  e.u.; for bromanil-KI,  $\Delta E^\ddagger = 9.8$  kcal/mole,  $\Delta S^\ddagger = -16.3$  e.u. Moreover, it was considered that 1) the electron donor is not a dissociated ion but the ion pair of alkali iodide. 2) a kind of charge transfer complex is formed as an intermediate in the electron transfer process and that 3) the rate of reaction is in the following order for the substituted halogen,  $F > Cl > Br > I$ . But the reaction rate can not be successfully explained in terms of electron affinity of the electron acceptor.

## Introduction

It has been found that in the aromatic substitution or addition reactions various types of intermediates such as  $\sigma$ -complex and charge-transfer complex ( $\pi$  or C-T complex) are formed, but the processes of formation and/or the disappearance of these intermediates have been hardly investigated in relation with the reactivity from the view point of kinetics.

The author has already reported on the kinetical study on the formation of  $\sigma$ -complex, *i.e.* Meisenheimer compound from 1,3,5-trinitrobenzene and an aliphatic amine, the whole reaction of which was pursued by means of the stopped flow method<sup>1)</sup>.

In general, the formation of C-T complex is very fast and the rate is nearly of vibrational frequency. The direct kinetic measurement of this rate process is out of the range of practical experiment but the complete electron transfer reaction is expected to be somewhat slower. These processes are important in organic reactions in the point that reactions proceed through the change of electron distribution, especially in the reaction taking place between the electron acceptor and the electron donor. The spectroscopic properties of the C-T complexes have been widely studied in relation to the electron affinity of the acceptor and the ionization potential of the donor in static state<sup>2)</sup>. The properties

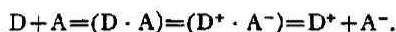
(Received August 26, 1969)

1) J. Osugi and M. Sasaki, *This Journal*, 37, 43 (1967)

2) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe", Springer-Verlag, Berlin (1961)

of C-T complexes as intermediates and the effects of that on the following reaction steps, that is, the way in which the C-T complex contributes to reaction rates have been little investigated.

The thermal electron transfer process takes place in a manner which can be rationalized as shown ;



One point which must be kept in mind is that the charge-transfer band for a neutral C-T complex may be hardly changed in energy upon the transfer of that complex from a nonpolar solvent to a polar solvent.

In 1954, Bijl *et al.* discovered that *N, N, N', N'*-tetramethyl-*p*-phenylenediamine (TMPD) and chloranil reacted rapidly to yield a solution which contained the radical cation, TMPD<sup>+</sup>, and semiquinone anion<sup>3)</sup>. After some confusion about the nature of the species in solution, the situation was clarified. In nonpolar solvents TMPD and even strong acceptors, *e.g.*, tetracyanoethylene (TCNE)<sup>4)</sup>, chloranil<sup>5)</sup> and tetracyanoquinodimethane<sup>6)</sup>, interact to form C-T complexes. In more polar solvents optical and ESR spectra pointed to partial or complete electron transfer with the formation of a radical cation and a radical anion.

The C-T complexes of tetrahalogeno-*p*-benzoquinones (halogenanils), tetracyanoethylene and trinitrobenzene (TNB) with alkali halides have been investigated in various media. Briegleb *et al.* found that the absorption maxima of the C-T bands of halogenanils, TCNE and TNB with alkali bromides is strongly solvent dependent and this was attributed to the strong solvation of the complex ions or complex ion pairs<sup>7,8)</sup>. But the alkali iodides as electron donors react with the powerful electron acceptors by complete electron transfer to form the corresponding radical anions of acceptors<sup>8)</sup>, and the absorption bands are in  $(22.4 \sim 24.2) \times 10^3 \text{ cm}^{-1}$ , somewhat in the longer wave length than those of the C-T complexes, the solvent effect of which is not so strong as the C-T complexes between these acceptors and alkali bromide.

In the present work, the author investigated the complete electron transfer reactions to produce semiquinone ion radicals from the halogenanils and alkali iodides in acetone solution by the spectrophotometric and ESR methods from the view point of kinetics, turning his attention to the following :

- 1) Though the C-T complexes and radical ions are in fact ionic in their character, it is obscure whether the donors are ionic dissociated ions or undissociated ion pairs.
- 2) As in the case of the TCNE-LiI system in acetonitrile<sup>9)</sup>, it is probable that the complete electron transfer reaction may take place through a kind of C-T complex as an intermediate.
- 3) Is it possible to explain the rate of complete electron transfer reactions in terms of the electron affinity of electron acceptors ?

3) D. Bijl, H. Kainer and A.C. Rose-Innes, *Naturwiss.*, **41**, 303 (1954)

4) W. Liptay, G. Briegleb and K. Schindler, *Z. Elektrochem.*, **66**, 331 (1962)

5) I. Isenberg and S.L. Baird, Jr., *J. Am. Chem. Soc.*, **84**, 3803 (1962)

6) R. Foster and T.J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962)

7) G. Briegleb, W. Liptay and R. Fick, *Z. Elektrochem.*, **66**, 851 (1962)

8) G. Briegleb, W. Liptay and R. Fick, *ibid.*, **66**, 859 (1962)

## Experimentals

### Materials

Tetrafluoro-*p*-benzoquinone (fluoranil): K & K Lab. reagent was purified by sublimation; mp. 290°C.

Tetrachloro-*p*-benzoquinone (chloranil): Commercial reagent was recrystallized from benzene; mp. 290°C.

Tetrabromo-*p*-benzoquinone (bromanil): It was synthesized from hydroquinone by bromination with Br<sub>2</sub> according to the method of Jackson and Bolton<sup>9</sup>, then recrystallized from benzene; mp. 300°C.

Tetraiodo-*p*-benzoquinone (iodanil): It was synthesized from chloranil and potassium iodide according to the method of Torrey and Hunter<sup>10</sup>, which was recrystallized from ethyl acetate; mp. 288°C.

Sodium iodide and potassium iodide: Commercial guaranteed reagents were dried in vacuum at 110°C for about 12 hrs just before the use.

Chloranil<sup>-</sup>-Na<sup>+</sup> salt: The saturated acetone solutions of both chloranil and NaI were mixed at 0°C and the greenish black precipitate was quickly filtered<sup>10</sup>, being dried in vacuum.

Chloranil<sup>-</sup>-K<sup>+</sup> salt: The fine powder of KI was added into the dry saturated acetone solution of chloranil and after gentle agitation, the liquid with light precipitate suspended was poured off upon filtration and after washing with more acetone and allowing it to dry<sup>10</sup>, it was found to be grass green.

Bromanil<sup>-</sup>-Na<sup>+</sup> salt: The bromanil suspended in acetone was mixed with the saturated acetone solution of NaI, after filtering, by pouring the quinone solution into the iodide solution. The reaction was instantaneous and the precipitate, almost black, was filtered off with suction<sup>10</sup>, being washed with ether and then was dried, kept pressed out, in a vacuum desiccator.

Bromanil<sup>-</sup>-K<sup>+</sup> salt: The mixing together of the suspended solutions of two compounds, bromanil and KI, with vigorous agitation gives readily green salt. The liquid with light precipitate was quickly filtered.

The acetone used as the solvent was dried with potassium carbonate and distilled immediately before the use, bp. 56.5°C.

### Apparatus and measurement of reaction rate

The rate of semiquinone formation was followed by the spectrophotometry at 443 mμ using the stopped flow apparatus described in the previous paper<sup>12</sup>. The reaction is not so fast that a recorder was used satisfactorily and the reaction rate was calculated from the initial slope of the curve of optical density against the reaction time. The complete mathematical formulation of the reaction rate over the whole reaction is not convenient and difficult to be evidenced experimentally, because of the occurrence of secondary slow reactions, perhaps the reduction of semiquinone or the substitution with iodide<sup>10</sup>.

9) C. L. Jackson and E. K. Bolton, *J. Am. Chem. Soc.*, **36**, 301 (1914)

10) H. A. Torrey and W. H. Hunter, *ibid.*, **34**, 708 (1912)

## Results

Of chloranil<sup>-</sup>-Na<sup>+</sup> salt and bromanil<sup>-</sup>-Na<sup>+</sup> salt, the infrared spectra were shown in Fig. 1 in KBr disc, which agree well with those from the corresponding Li salts observed by Matsunaga<sup>11)</sup>. In stead of the normal CO stretching vibration of *p*-chloranil at 1,690 cm<sup>-1</sup> a strong absorption band is observed at 1,530 cm<sup>-1</sup>, and in *p*-bromanil the absorption at 1,680 cm<sup>-1</sup> shifts to 1,510 cm<sup>-1</sup> in Na salt. Almost the same spectra have been observed for K salts. As the frequency of the CO stretching vibration is known to be mainly determined by the bond order, the observed shifts can be attributed to the acceptance of one electron into the antibonding level of the quinone, so that the CO bond loses to some extent the double bond character and the ring loses the quinoid character. The electronic spectra of the solid chloranil<sup>-</sup>-Na<sup>+</sup> salt dissolved in acetone and that of dilute solution of chloranil mixed with NaI were illustrated in Fig. 2. These two spectra are well coincident, showing absorption maxima at 420 and 450 m $\mu$ . For other salts, the electronic spectra were almost analogous and showed the absorption band between 400 and 500 m $\mu$ . Foster found that chloranil<sup>-</sup>-Na<sup>+</sup> gives the absorption at 426 m $\mu$  and 450 m $\mu$  in alcohol<sup>12)</sup> and these can be considered to correspond to the absorption bands at 410 and 430 m $\mu$  of *p*-benzosemiquinone ion radical in aqueous solution<sup>13) 14)</sup>. The difference in transition energy may be attributed mainly to the large electron affinity of the halogenanils compared with

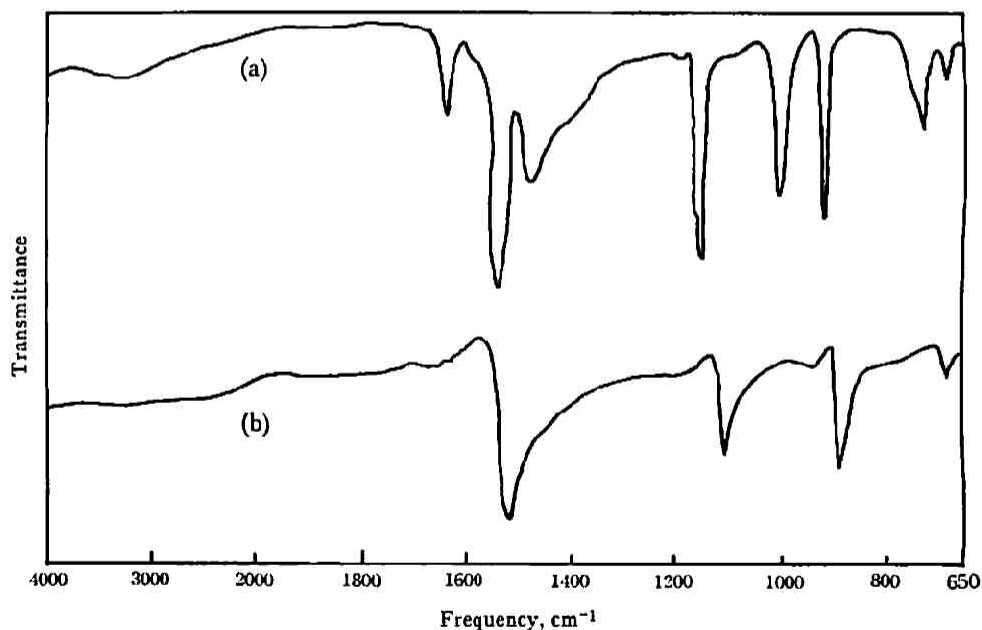


Fig. 1 The infrared spectra of semiquinone ion radical salts in KBr disc

(a) chloranil<sup>-</sup>-Na<sup>+</sup>

(b) bromanil<sup>-</sup>-Na<sup>+</sup>

11) Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964)

12) R. Foster and T.J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962)

13) M. Eigen and P. Matthies, *Chem. Ber.*, **94**, 3309 (1961)

14) H. Diebler, M. Eigen and P. Matthies, *Z. Naturforsch.*, **16 b**, 629 (1961)

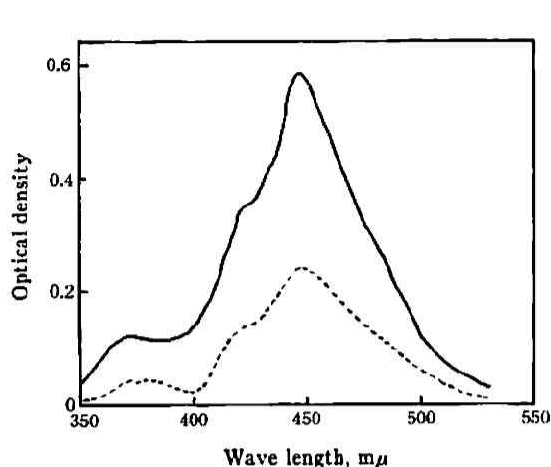


Fig. 2 The electronic spectra of chloranil-  
—Na<sup>+</sup> in acetone

—: acetone solution of solid chloranil-  
—Na<sup>+</sup> prepared previously  
...: dilute solution of chloranil imme-  
diately after mixing together with  
dilute solution of NaI

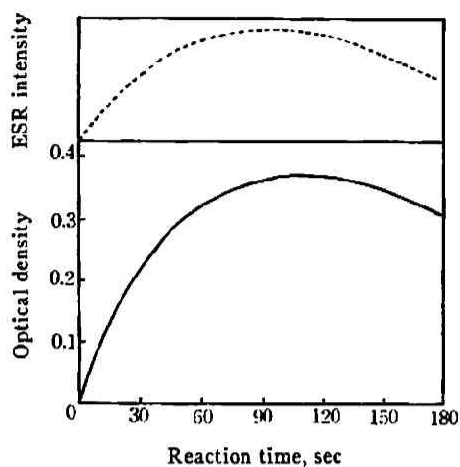


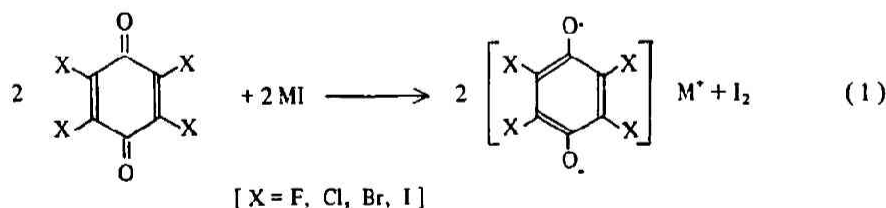
Fig. 3 The changes of optical density at  
443 mμ and ESR spectrum with  
time at 30°C

[chloranil]<sub>0</sub> = 3.5 × 10<sup>-4</sup> (mole/l),  
[NaI]<sub>0</sub> = 1.0 × 10<sup>-2</sup> (mole/l)  
—: optical density  
.....: ESR signal intensity

nonsubstituted *p*-benzoquinone.

The electron spin resonance spectra of acetone solutions of chloranil and bromanil mixed with NaI were observed and a sharp singlet line was observed in each case, the *g*-values of which are 2.004 and 2.007, respectively, these values being in good agreement with those obtained by Kainer.<sup>15)</sup>

The reaction of halogenanils with alkali iodides in acetone or in acetonitrile is well known as a popular method to prepare the corresponding semiquinone ion radicals.



The formation can be represented as reaction (1)<sup>10)</sup> but alkali iodides are partly dissociated into ions in solution, especially in high dielectric medium, and so the following reactions must be kept in mind together with reaction (1).



If the molecular extinction coefficients of semiquinone,  $\text{I}_2^-$  and  $\text{I}_3^-$  are represented by  $\epsilon_1$ ,  $\epsilon_2$  and  $\epsilon_3$

15) H. Kainer, D. Bijl and A. C. Rose-Innes, *Nature*, **178**, 1462 (1956)

respectively under the usage of a filter at 443 m $\mu$  whose  $\Delta\lambda_{1/2}$  is about 8 m $\mu$ , the optical density can be described as follows ;

$$D_{\text{obs}} = \left\{ \epsilon_1 + \frac{\epsilon_2 + \epsilon_3 K_2 [I^-]}{2(1 + K_2 [I^-])} \right\} l [\text{SQ}^-], \quad (4)$$

where  $l$  is the optical path length. In acetone  $\epsilon_2$  and  $\epsilon_3$  are nearly equal, about 800, and the values of  $K_1$  and  $K_2$  were cited :

$$K_1 = 6.3 \times 10^{-3} (\text{l/mole}) \text{ for NaI}^{16) 17)}, K_1 = 9.0 \times 10^{-3} (\text{l/mole}) \text{ for KI}^{17) \sim 19)}$$

and  $K_2 = 10^{8.2} (\text{l/mole})^{20)}$ .

When the concentration of NaI is  $10^{-2} \sim 10^{-3}$  (mole/l), the condition  $K_2 [I^-] \gg 1$  may be satisfied and equation (4) can be approximated to equation (5)

$$D_{\text{obs}} = (\epsilon_1 + \epsilon_3/2) l [\text{SQ}^-] = \epsilon l [\text{SQ}^-]. \quad (5)$$

The values of  $\epsilon_1 l$  and  $\epsilon_3 l$  were practically measured in the flow apparatus. Changes of intensities of optical density and ESR signal with the reaction time were compared with each other in Fig. 3 at 30°C under the condition that  $[\text{chloranil}] = 3.5 \times 10^{-4}$  (mole/l) and the initial stoichiometric concentration of NaI,  $[\text{NaI}]_{\text{T.O.}} = 1.0 \times 10^{-2}$  (mole/l). Both changes are well parallel in the initial reaction stage but after a time the reaction is complicated, accompanied by the disappearance of semiquinone. The change of intensity of ESR signal was obtained by fixing the magnetic field at the maximum peak.

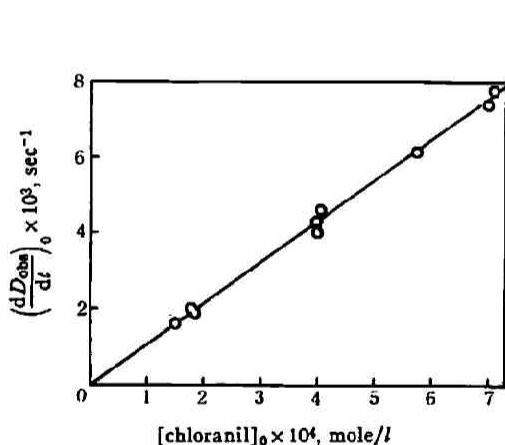


Fig. 4 The dependency of the initial reaction rate on  $[\text{chloranil}]_0$  at 30°C under the constant stoichiometric concentration of NaI,  $6.05 \times 10^{-3}$  (mole/l)

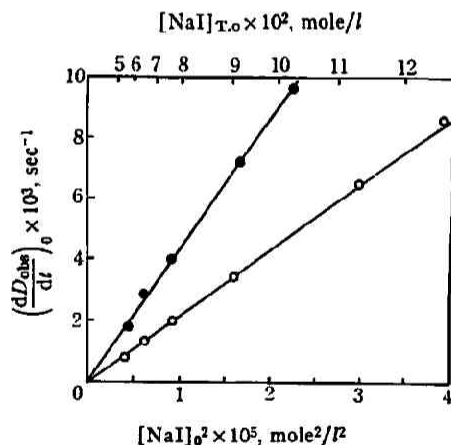


Fig. 5 The dependency of the initial reaction rate on  $[\text{NaI}]$  at 30°C under the constant initial concentration of chloranil

○ :  $[\text{chloranil}]_0 = 1.83 \times 10^{-4}$  (mole/l)  
 ● :  $[\text{chloranil}]_0 = 3.58 \times 10^{-4}$  (mole/l)

- 16) J.F.J. Dippy, H.O. Jenkins and J.E. Page, *J. Chem. Soc.*, **1939**, 1386
- 17) G.J. Janz and M.J. Tait, *Can. J. Chem.*, **45**, 110 (1967)
- 18) M.B. Reynold and C.A. Krans, *J. Am. Chem. Soc.*, **70**, 1708 (1948)
- 19) J.F.J. Dippy and S.R.C. Hughes, *J. Chem. Soc.*, **1954**, 953
- 20) I.V. Nelson and R.T. Iwamoto, *J. Electroanal. Chem.*, **7**, 218 (1964)

But it was too difficult to obtain the reproducible data over every experimental run, and the rate was measured only according to the photometric method.

The dependence of the initial rate of semiquinone formation on chloranil was shown in Fig. 4 under constant initial concentration of NaI. On the other hand, the dependence on [NaI] was found in Fig. 5, where the upper abscissa is the scale of the initial stoichiometric concentration of NaI and the lower,  $[\text{NaI}]_0$ , is the concentration of undissociated ion pair when prepared.  $[\text{NaI}]_0$  was calculated from  $[\text{NaI}]_{T,0}$  using the values of  $K_1$  and  $\Delta H^\circ = -3.0$  (kcal/mole)<sup>21)</sup>, at each temperature.

From these figures, it can be concluded that the initial reaction rate is of first order with respect to chloranil and of second order for NaI, that is,

$$\left(\frac{d[\text{Cl}_4\text{SQ}^-]}{dt}\right)_0 = k_{app}[\text{chloranil}]_0[\text{NaI}]_0^2. \quad (6)$$

The analogous relations were also allowed to be applied to the systems, such as chloranil-KI, bromanil-KI, fluoranil-NaI and iodanyl-NaI. All these results obtained are shown in Figs. 6~10. When potassium iodide was used,  $[\text{KI}]_0$  was also calculated from  $[\text{KI}]_{T,0}$  using the values of  $K_1$  and  $\Delta H^\circ = -3.0$  (kcal/mole).

In both the cases of fluoranil-NaI and iodanyl-NaI, the reliable results can not be obtained perhaps because, in the case of fluoranil-NaI, the semiquinone ion radical formed is rather unstable and because, in the case of iodanyl-NaI, the reaction is too slow compared with the stability of the apparatus.

The apparent third order rate constant,  $k_{app}$ , calculated from the slopes of Figs. 6~10 were given on Table 1. From the dependence of  $k_{app}$  on temperature as shown in Fig. 11, the energies of acti-

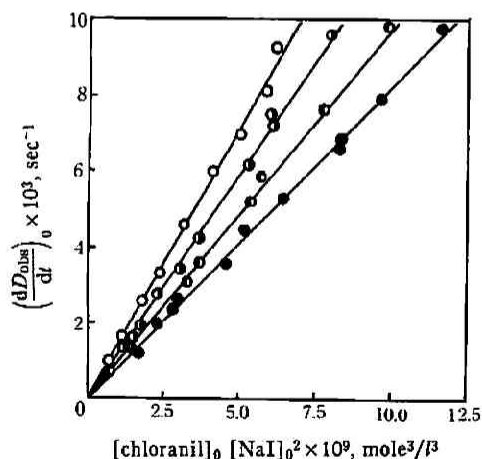


Fig. 6 The dependency of the initial reaction rate on the concentrations at various temperatures in chloranil-NaI system

●: 20°C    ◐: 25°C  
◑: 30°C    ○: 35°C

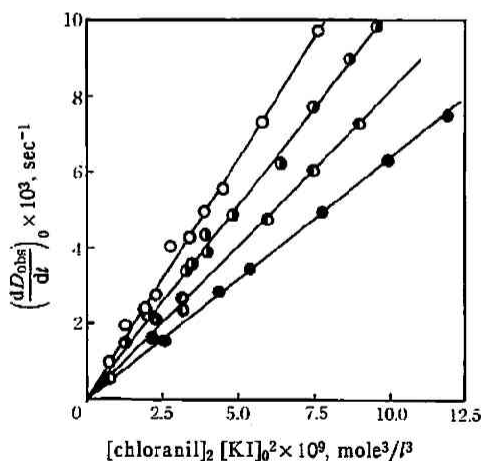


Fig. 7 The dependency of the initial reaction rate on the concentrations at various temperatures in chloranil-KI system

●: 20°C    ◐: 25°C  
◑: 30°C    ○: 35°C



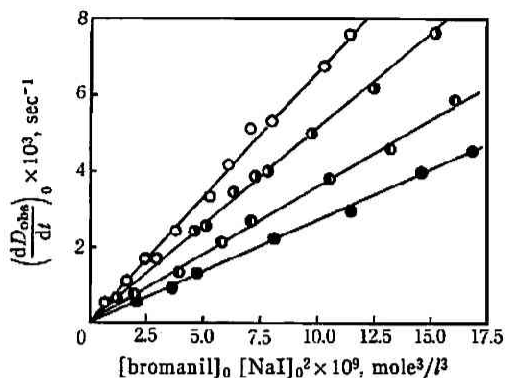


Fig. 8 The dependency of the initial reaction rate on the concentrations at various temperatures in bromanil-NaI system

●: 20°C    ◐: 25°C  
◑: 30°C    ○: 35°C

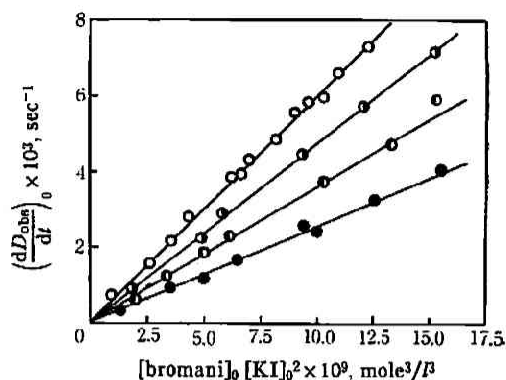


Fig. 9 The dependency of the initial reaction rate on the concentrations at various temperatures in bromanil-KI system

●: 20°C    ◐: 25°C  
◑: 30°C    ○: 35°C

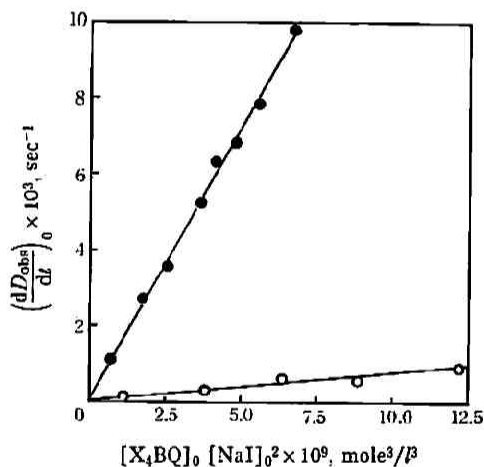


Fig. 10 The dependency of the initial reaction rate on the concentrations at 30°C in fluoranil-NaI and in iodanyl-NaI system

●: fluoranil-NaI  
○: iodanyl-NaI

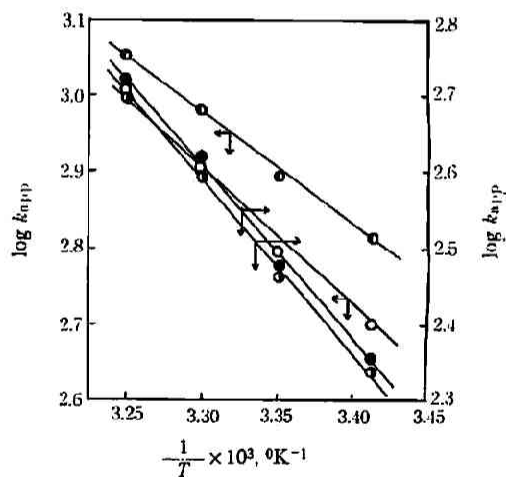


Fig. 11 The Arrhenius plots of  $k_{app}$

●: chloranil-NaI  
●: bromanil-NaI  
○: chloranil-KI  
○: bromanil-KI

vation and the entropies of activation were calculated and given on Table 2.

### Discussions

It must be considered whether the electron donor is the dissociated iodide ion or undissociated ion pair of alkali iodides. For the C-T complex formation between TNB and LiI and LiBr in

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Table 1 The apparent third order rate constants on the semiquinone ion radical formation reactions from halogenanils

	$k_{\text{app}}$ ( $\text{l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ )			
	20°C	25°C	30°C	35°C
fluoranil-NaI <sup>a)</sup>			1,200	
chloranil-NaI <sup>a)</sup>	660	780	956	1,130
chloranil-KI <sup>b)</sup>	500	628	832	1,000
bromanil-NaI <sup>c)</sup>	229	300	420	528
bromanil-KI <sup>d)</sup>	225	295	392	516
iodanil-NaI <sup>e)</sup>			68	

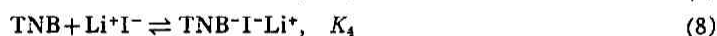
a) calculated from equation (5) using  $\epsilon l = 1.230$  b)  $\epsilon l = 1.270$  c)  $\epsilon l = 1.167$  d)  $\epsilon l = 1.120$ e) The accurate values of  $\epsilon l$  could not be obtained and so calculated assuming  $\epsilon l = 1.200$ 

Table 2 The activation parameters on the semiquinone ion radical formation reactions

	$\Delta E^\ddagger$ (kcal/mole)	$\Delta H^\ddagger$ (kcal/mole) <sup>a)</sup>	$\Delta S^\ddagger$ (e.u.)	$\Delta G^\ddagger$ (kcal/mole) <sup>b)</sup>
chloranil-NaI	6.8	6.2	-19.4	12.0
chloranil-KI	7.6	7.0	-18.6	12.6
bromanil-NaI	9.7	9.1	-16.6	14.1
bromanil-KI	9.8	9.2	-16.3	14.1

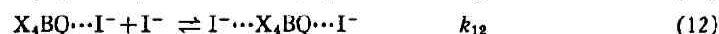
a)  $\Delta H^\ddagger = \Delta E^\ddagger - RT$ , at  $T = 300^\circ\text{K}$ b)  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ , at  $T = 300^\circ\text{K}$ 

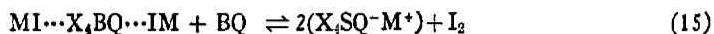
acetonitrile (dielectric constant,  $\text{DK} = 37.5$ ), both reactions (7) and (8) have been considered to take place <sup>7)</sup>.



on the assumption,  $K_3 \approx K_4$ . On the other hand in the medium of low dielectric constant, *e.g.*, in *iso*-propanol, reaction (8) was only considered. But in tetrahydrofuran ( $\text{DK} = 7.6$ ), the anion of TCNE and triiodide ion were detected in the reaction of TCNE with  $\text{LiI}$ , and the formation of  $\text{TCNE} \cdots \text{I}^-$  complex, a kind of the C-T complex where iodide ion acts as an electron donor, was expected to precede the complete electron transfer<sup>8)</sup>.

In the present case, using acetone as solvent ( $\text{DK} = 21.4$ ), the possibility of the contribution of both the pair and the dissociated ion as a donor should be considered and so the following reaction scheme can be constructed.

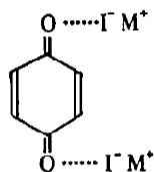




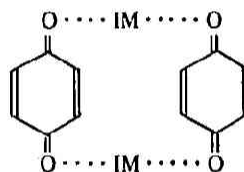
Here,  $X_4BQ \cdots IM$  and  $X_4BQ \cdots I^-$  can be regarded as the C-T complexes. Besides, the following equilibrium (18) may exist,



but as it does not influence on the kinetical treatment,  $X_4BQ \cdots IM$  expresses here that formed from ion pair  $MI$ , not from free ion  $I^-$ . In reactions (11)~(14) the intermediate complexes,  $I^- \cdots X_4BQ \cdots IM$ ,  $I^- \cdots X_4BQ \cdots I^-$  and  $IM \cdots X_4BQ \cdots IM$ , may be formed by the addition of donors at the local site, the oxygen atoms of the acceptor as seen in (I) rather than the partial electron transfer into the delocalized molecular orbital, and the addition of the second donor is considered to be the rate determining step. Reactions (15)~(17) may be fast and proceed passing through the state as seen in (II) which is also considered to be a kind of the dimer of the C-T complex<sup>29</sup>.



(I)



(II)

The initial rate of the semiquinone ion radical formation,  $v_0$ , can be expressed as equation (19),

$$v_0 = \left\{ \frac{k_{11}K_9[MI]_0^2 + k_{13}K_9[MI]_0[I^-]_0 + k_{12}K_{10}[I^-]_0^2 + k_{14}K_{10}[I^-]_0[MI]_0}{1 + K_9[MI]_0 + K_{10}[I^-]_0} \right\} [BQ]_0 \quad (19)$$

If the rate of formation of  $I^- \cdots X_4BQ \cdots IM$  is equal, independent of the reaction pathway and if the formation constants of the C-T complexes,  $I^- \cdots X_4BQ$  and  $X_4BQ \cdots IM$  are nearly equal, i.e.,  $K_9 \simeq K_{10}$  as assumed in the case of TNB and  $LiI^{29}$  the relation,  $k_{13} \simeq k_{14}$ , results and the following equation can be derived using the relationship,  $[I^-]_0 = K_1^{1/2}[MI]_0^{1/2}$ ,

$$v_0 = \left\{ \frac{k_{11}K_9[MI]_0 + 2k_{13}K_1^{1/2}K_9[MI]_0^{1/2} + k_{12}K_1K_9}{1 + K_9[MI]_0 + K_1^{1/2}K_9[MI]_0^{1/2}} \right\} [MI]_0[BQ]_0 \quad (20)$$

If the assumption,  $K_9[MI]_0 \ll 1$  is satisfied under the experimental condition,  $[MI]_0 \approx 10^{-2} \sim 10^{-3}$  (mole/l), the relationship,  $K_1^{1/2}K_9[MI]_0^{1/2} \ll 1$  can be allowed and equation (21) can be deduced from equation (20).

$$v_0 = (k_{11}K_9[MI]_0 + 2k_{13}K_1^{1/2}K_9[MI]_0^{1/2} + k_{12}K_1K_9)[MI]_0[BQ]_0 \quad (21)$$

If the assumptions mentioned above were not satisfied or if the values of  $k_{11}$ ,  $k_{12}$  and  $k_{13}$  were not negligible, same order of magnitude, neither equations (19) and (20) nor equation (21) could explain the simple experimental relationship, equation (5). So either of the assumptions described below has to be considered.

i)  $K_9 \simeq K_{10}$  and  $k_{11} \gg k_{12}, k_{13}, k_{14}$

ii)  $K_9 \gg K_{10}$  and  $k_{11} \gg k_{13}$

It is impossible, for the present, to discuss which assumption is appropriate, but Briegleb *et al.* postulated assumption i) in the reaction between TNB and LiI<sup>7)</sup>. In any case, equation (21) can be reduced to equation (22).

$$\frac{d[X_4SQ^-]}{dt} = k_{11}K_9[MI]_0^2[BQ]_0. \quad (22)$$

$$k_{app} = k_{11}K_9 \quad (23)$$

When chloranil is mixed with NaI in acetone at  $-78^\circ\text{C}$ , greenish yellow color is instantaneously developed and soon fades to yellow. The component showing green color, although its spectrum can not be obtained, can be assigned to the complex,  $\text{NaI} \cdots \text{Cl}_4\text{BQ}$ , analogous to  $\text{TCNE} \cdots \text{I}^-$  complex in the reaction between TCNE and LiI in the acetonitrile which is expected to have the absorption maximum near  $660 \text{ m}\mu$ . In this work, the change of optical density at  $660 \text{ m}\mu$  was followed and was traced on the oscillograph. The displacement of optical density with time was very small, but the rough value of  $k_{11}$  was determined when  $[\text{chloranil}]_0 = 2 \times 10^{-5} \text{ (mole/l)}$  and  $[\text{NaI}]_0 = (4 \sim 12) \times 10^{-4} \text{ (mole/l)}$ , assuming that a pseudo-first order rate equation is satisfied with respect to the complex, that is,

$$\frac{d[\text{Cl}_4\text{BQ} \cdots \text{INa}]}{dt} = -k_{11}[\text{NaI}]_0[\text{Cl}_4\text{BQ} \cdots \text{INa}]. \quad (24)$$

$$k_{11} \simeq 5 \times 10^4 \text{ (l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1})$$

For bromanil-NaI and chloranil-KI systems the analogous measurements were tried but only much less accurate values were obtained, and so the quantitative comparison was impossible.

The rate constant of semiquinone ion radical formation by the electron transfer from alkoxy ion to 2-chloro-*p*-benzoquinone was found to be more than  $4.3 \times 10^3 \text{ (l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1})$  at  $20^\circ\text{C}$ <sup>22)</sup> and much larger value is expected for chloranil, perhaps more than  $10^4$ . It is impossible to distinguish from the comparison of these rate constants whether the donor is a dissociated ion or an undissociated ion pair, because the various experimental condition, including acceptors and solvents, are different. But it may be safely concluded that the reaction takes place between the acceptor and the undissociated ion pair of alkali iodide for the reasons that 1) the apparent reaction rate is higher for NaI than for KI in spite of the fact that the dissociation constant of them are *vice versa*, and 2) the rate is expressible by the formula (6) or (22) which is not allowed by considering the dissociated ion as the donor.

The apparent activation energies are divided into two terms, taking equation (23) into consideration,

$$\Delta E^* = \Delta E_{11}^* + \Delta H_9^0, \quad (25)$$

where  $\Delta H_9^0$  is the enthalpy change accompanying equilibrium (9). The enthalpy change accompanying a C-T complex formation is, in general, increased with increasing electron affinity (E.A.) of an acceptor if a donor is fixed<sup>23)</sup>.

22) M. Sasaki, *This Journal*, 39, 40 (1969).

The electron affinities of halogenanils are cited below.

E.A. (chloranil):	4.16 (eV) <sup>23)</sup> ,	2.59 (eV) <sup>24)</sup>
E.A. (bromanil):	4.32 (eV) <sup>23)</sup> ,	2.62 (eV) <sup>24)</sup>
E.A. (iodanil) :		2.55 (eV) <sup>24)</sup>

The MO calculation also gives the strong electron affinity to bromanil than to chloranil<sup>25)</sup>. So  $\Delta E^*$  listed on Table 2 can neither be only explained in terms of  $\Delta H_s^0$ , nor the rate constant can be explained in terms of pre-equilibrium constant,  $K_p$ .

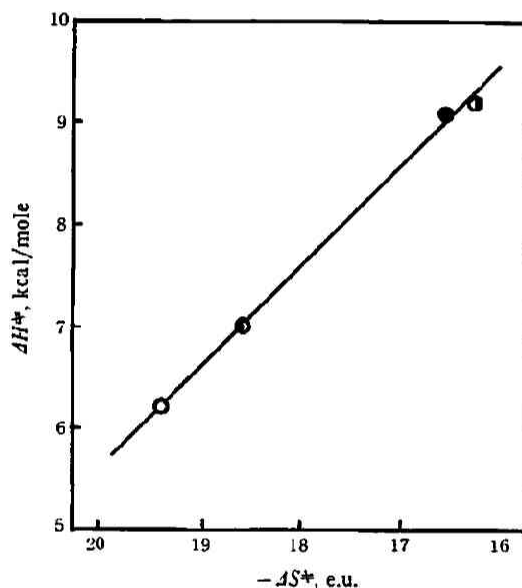


Fig. 12 Linear free energy relationship

○: chloranil-NaI  
 ●: bromanil-NaI  
 ◐: chloranil-KI  
 ◑: bromanil-KI

The linear free energy relationship was satisfied in a series of reactions as shown in Fig. 12, in which the slope of the line gives the isokinetic temperature<sup>26)</sup>,  $\beta=1,020$  (°K). Although the range of variation of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  is so small that the correlation coefficient,  $\beta$ , contains great error, the reactions probably take place according to the same reaction mechanism. Considering that  $\beta$  is much larger than room temperature, the reaction may be of enthalpy- or energy-controlling at room temperature and not only the enthalpy change  $\Delta H_s^0$  but also the energy of activation in reaction (11) should be considered to be important. The predominant factor contributing to the activation is probably not the electron affinity of halogenanils but the local inductive effect due to the substituted halogens.

23) R. Foster, *Tetrahedron*, **10**, 96 (1960)

24) M. Batley and L.E. Lyons, *Nature*, **196**, 573 (1962)

25) S.A. Berger, *Spectrochimica Acta*, **23 A**, 2213 (1967)

26) J.E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", p. 324, John Wiley and Sons, Inc., New York and London (1963)

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